AMPEROMETRIC TITRATION OF METAL IONS WITH EDTA. THE ANALYTICAL APPLICATION OF THE OXIDE ELECTRODE

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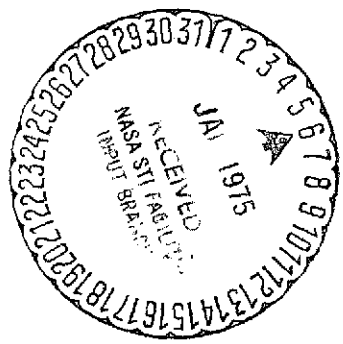

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16. Abstract

In the amperometric titration of metal ions with EDTA, an oxide electrode is employed (a platinum electrode coated with an oxide layer; e.g., with Tl_2O_3 or Ni_2O_3, Co_2O_3, MnO_2, PbO_2, PtO_2, Bi_2O_3). These electrodes are active and stable over a relatively wide range of pH and will react to an excess of EDTA (after the equivalence point). The procedures are specified a) for determining individual metal ions, and b) for determining 2 ions when present together. In the case b) we apply the principle that the stability of metal-EDTA complexes is a function of the pH of the solution. First a pH is chosen such that only one ion forms a stable complex (stability constant greater than 10^7). This ion can then be titrated with EDTA without interference from the other ion. Next the pH is adjusted so that the 2nd ion also forms a suitably stable complex.

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AMPEROMETRIC TITRATION OF METAL IONS WITH EDTA. THE ANALYTICAL APPLICATION OF THE OXIDE ELECTRODE***

Gerald Kainz and Gerhard Sontag*

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Summary: In the amperometric titration of metal ions with EDTA, an oxide electrode is employed (a platinum electrode coated with an oxide layer; e.g., with Tl_2O_3 or Ni_2O_3, Co_2O_3, MnO_2, PbO_2, PtO_x, Bi_2O_5). These electrodes are active and stable over a relatively wide range of pH and will react to an excess of EDTA (after the equivalence point). The procedures are specified a) for determining individual metal ions, and b) for determining 2 ions when present together. In the case b) we apply the principle that the stability of metal-EDTA complexes is a function of the pH of the solution. First a pH is chosen such that only one ion forms a stable complex (stability constant greater than 10^7). This ion can then be titrated with EDTA without interference from the other ion. Next the pH is adjusted so that the 2nd ion also forms a suitably stable complex.

We have previously shown [1, 2] that it is possible to perform a direct amperometric indication of EDTA by utilizing an oxide-coated platinum anode and a bare platinum cathode and applying a polarization current of approximately 1 V. When an excess of EDTA is added during the titration, the current flowing between the electrodes increases sharply. Suitable oxides are the

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** Numbers in margin indicate pagination in original foreign text.

*** Respectfully and gratefully dedicated to Dr. Friedrich Hecht on his 70th birthday.

oxides of trivalent thallium, nickel, and cobalt, the oxides of quadrivalent lead and manganese or platinum, and the oxide of quinquevalent bismuth. The preparation and the properties of these oxide electrodes were researched, as were the causes of the galvanic reaction.

In this paper we have investigated the extent to which these oxide electrodes could be used in practice in the titration of metal ions with EDTA.

The following conditions must be fulfilled in the titration:

1. The pH of the solution must be such that the metal chelate which forms during titration is sufficiently stable (log K_{eff} greater than 7). 2. An oxide electrode must be chosen which shows a maximal indication at the pH chosen, since the change of current caused by EDTA depends upon both the pH of the solution and the type of oxide employed. First we shall discuss the determination of individual metal ions.

I. DETERMINATION OF INDIVIDUAL METAL IONS

Table 1 (a) lists the ions which can be directly chelatometrically titrated with the aid of the oxide electrode. The corresponding titration curve is shown in Figures 1 and 2; see note.

Table 1 (b) lists the ions which require the addition of excess EDTA. This excess is then back-titrated with a standard solution of zinc (II) (Figure 3). This measure is necessary because the complexformation proceeds particularly slowly. In direct titration, slowly reacting ions are present if the addition of excess EDTA causes the current to increase and then return to its basic level. These ions include Cr^{3+}, Hf^{4+}, TiO^{2+}, VO^{2+}, Zr^{4+}; (these are not listed in Table 1).

Table 1 (c) lists ions which can likewise be determined only if back-titration is employed. In direct titration, oxide would separate from the anode and the resulting current would interfere in the indication of EDTA by the oxide electrode.

Other ions which can be determined with EDTA are: Ag^{+}, Fe^{2+}, Pd^{2+}, Sn^{2+} and the rare earths. It seems possible to use an oxide electrode as an indicator. Either direct or indirect titration may be employed, depending upon the speed of the reaction.

II. DETERMINATION OF ION COMBINATIONS

Previously only a few ion combinations in a solution could be determined by using color indicators (see Schwarzenbach [4]). In this respect the oxide electrodes are far superior to color indicators, because they can be employed over a wider range of pH, and they do not change the test solution. It is not difficult to determine 2 ions when present together, provided a suitable pH is chosen. The first step is to choose a pH such that only one ion forms a stable complex (log K_{eff} greater than 7), while the second ion forms a less stable complex (log K_{eff} less than 7). As a result only one ion is complexed by EDTA. Next the pH is adjusted such that the second ion also forms a stable complex (log K_{eff} greater than 7) and this second ion is then titrated. / 269

Consider the example of titration Fe-Zn (see Figure 4). At pH 2, log K_{eff} for iron (III) equals 11.5; for zinc (II), 3.8. If EDTA is added at pH 2, only the iron (III) is complexed; the current between the electrodes then increases sharply, as if free EDTA were present. The solution is then brought to pH 4.5. K_{eff} for zinc (II) now equals 7.9, and the zinc can also be titrated with EDTA.

A number of ion combinations have been determined in this manner, and we have found that this principle can be applied in a great many ways.

Table 2 includes the ion combinations which can be determined in a solution through direct titration. Table 3 lists the ion combinations which cannot be determined consecutively, because the formation constants of these ions are too similar. The difference between their log K_{eff} values should be 5, and certainly no less than 3. Table 4 includes the ion combinations in which one ion must be determined through back-titration. Naturally, this technique is not so precise as direct titration. Finally, Table 5 lists those combinations in which the formation constants of the ions are sufficiently different, but which cannot be determined experimentally. The reasons for this are given in the notes.

If one wishes to look up a particular ion combination, he should refer to Table 2. If the combination is not listed, he should consult the other tables in the order in which they appear. The ions are arranged alphabetically by chemical symbol. The ions Ga, In, Sc, and Y were not listed. If necessary, one must decide from the K_{eff} values whether a determination in the presence of another ion is possible. /270

III. INVESTIGATIONS OF POSSIBLE APPLICATIONS

We shall discuss some other properties of the oxide electrodes which pertain to their analytical application.

1. Influence of Excess EDTA

This case occurs during back-titration, when an excess of EDTA is added and then back-titrated with, e.g., a solution of zinc (II).

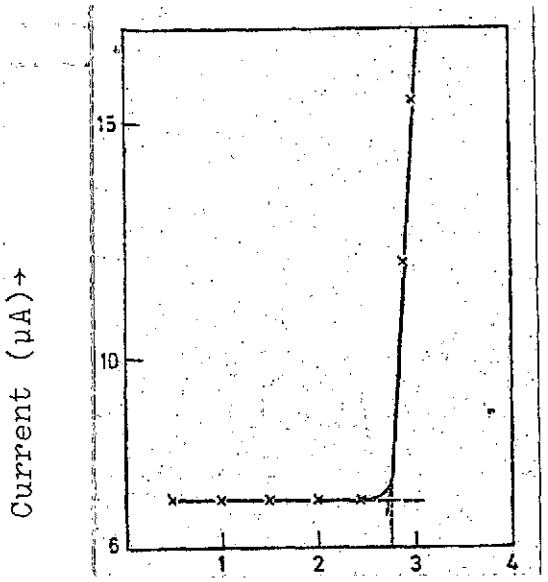

Figure 1. Titration of Ca^{2+} with EDTA (pH 10, Tl_2O_3 electrode, E = 1.1 V).

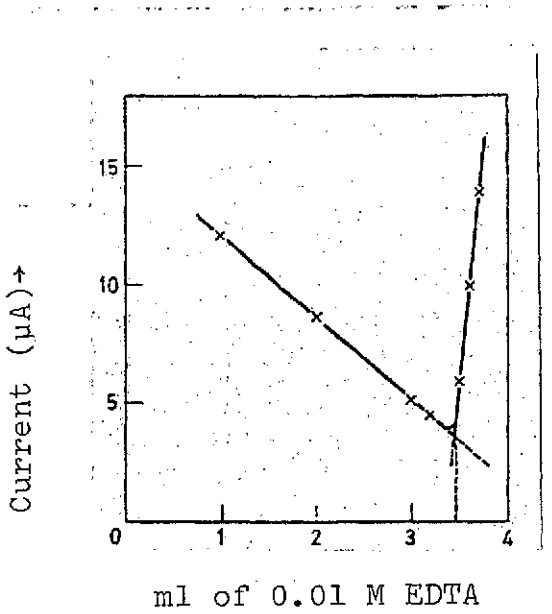

Figure 2. Titration of Cu^{2+} with EDTA (pH 10, Tl_2O_3 electrode, E = 1.1 V).

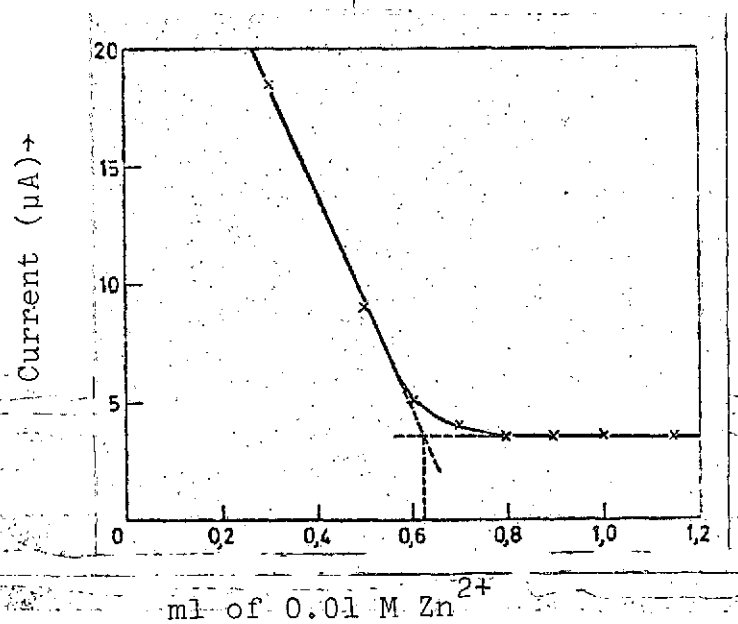

Figure 3. Back-titration of Al^{3+} with Zn^{2+} (pH 4.5, PbO_2 electrode, E = 1.1 V)

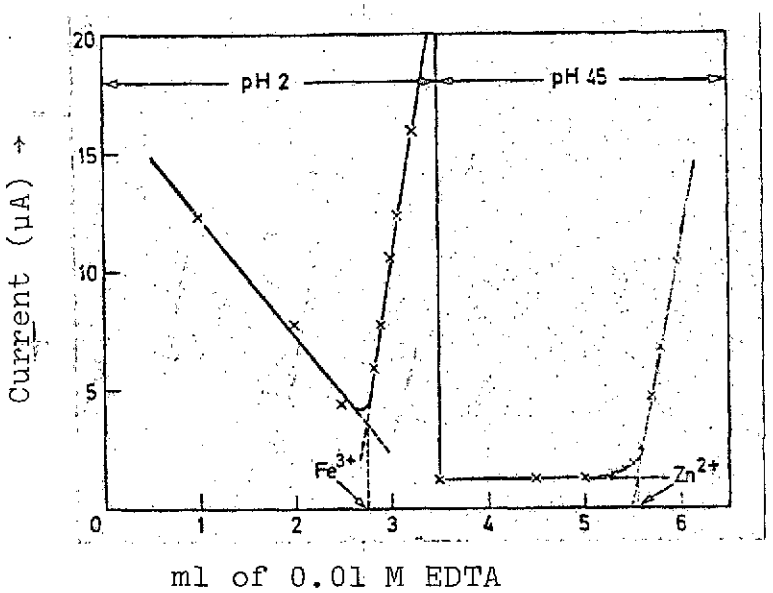

Figure 4. Consecutive titration Fe-Zn (pH_1 2.0; pH_2 4.5; MnO_2 electrode, E = 1.0 V)

TABLE I *

a) DIRECT TITRATION

Ion	pH	log K_{eff}	Electrode	Note
Ba^{2+}	10	7,3	Tl_2O_3	3
Bi^{3+}	2	8,6	MnO_2	3
Ca^{2+}	10	10,2	Tl_2O_3	3
Cd^{2+}	5	10,0	PbO_2	3
	10	15,5	Tl_2O_3	3
Ce^{3+}	4,5	7,4	PbO_2	3
Co^{2+}	4,5	8,8	PbO_2	1, 2, 3
Cu^{2+}	4,5	11,2	PbO_2	4
	10	16,6	Tl_2O_3	4
Fe^{3+}	2	11,5	MnO_2	4
Ga^{3+}	2	7,3	MnO_2	3
Hg^{2+}	4,5	11,3	PbO_2	4
In^{3+}	2	11,9	MnO_2	3
La^{3+}	4,5	7,8	PbO_2	3
Mg^{2+}	10	8,2	Tl_2O_3	3
Ni^{2+}	4,5	11,1	PbO_2	3
	10	17,4	Tl_2O_3	3
Pb^{2+}	4,5	10,4	PbO_2	2, 3
Sc^{3+}	4,5	15,1	PbO_2	3
Sr^{2+}	10	8,1	Tl_2O_3	3
Th^{4+}	2	9,5	MnO_2	3
Tl^{3+}	2	8,6	MnO_2	4
Y^{3+}	4,5	10,1	PbO_2	3
Zn^{2+}	4,5	8,9	PbO_2	3
	10	13,6	Tl_2O_3	3

b) BACK-TITRATION DUE TO ANODIC REACTION

Ion	pH of back-titration	log K_{eff}	Electrode	Note
Al^{3+}	4,5	8,6	MnO_2	5

c) BACK-TITRATION DUE TO ANODIC REACTION

Ion	pH of back-titration	log K_{eff}	Electrode	Note
Co^{2+}	10	14,7	Tl_2O_3	6
Mn^{2+}	10	13,4	Tl_2O_3	7
Pb^{2+}	10	14,8	Tl_2O_3	6

* Translator's note: Commas in numbers represent decimal points.

Notes on Table I

Note 1. The titration must be performed slowly because the complex formation proceeds slowly.

Note 2. During the titration some oxide separates from the anode. This reduces the increase in current after the equivalence point.

Note 3. Titration curve as in Figure 1.

Note 4. Titration curve as in Figure 2.

Note 5. Titration curve as in Figure 3.

Note 6. This ion can also be titrated directly (see (a)). However, some oxide separates from the anode, thereby reducing the increase in current after the equivalence point.

Note 7. Mn^{2+} can only be determined at pH 10 (through back-titration with zinc (II)). Due to the stability constant the back-titration could be performed at pH 6, but this has resulted in an error of +2% (insufficient consumption of zinc (II)).

Figure 5, No. 1, shows the following: a) There is a range within which the addition of EDTA causes an increase in current. Within this range EDTA is oxydized at the oxide anode, and in the process the anode is partially reduced. Current flows when the reduced areas are reoxydized. b) There is also a range within which the addition of EDTA causes the current to fall. We assume that higher concentrations of EDTA will block the oxide anode by preventing reoxydation of the reduced areas. The blockage disappears when the anode is dipped into a pure buffer solution and the current is switched on for about five minutes. The regenerated electrode then continues to indicate EDTA normally.

2. Influence of Ascorbic Acid

In some determinations (e.g., V^{5+} and UO^{2+}) ascorbic acid can serve as a reducing agent. Since an excess of ascorbic acid is always employed, we performed tests to determine whether or not this substance will harm the oxide electrode. We found that the current between the electrodes increases when ascorbic acid is added. This is due to the fact that ascorbic acid produces reduced areas on the oxide anode, which are then reoxidized on the anode. The more reduced areas are present at any one time, the higher is the current between the electrodes. A certain volume of ascorbic /273 acid — in this case 16 ml of 0.01 M solution — will dissolve the oxide layer and render the electrode inactive.

Ascorbic acid also has other disadvantages. For example, the signal for a particular concentration of EDTA becomes smaller as more ascorbic acid is present in the solution. The concentration of this acid must therefore be kept to an absolute minimum. SO_2 would be an even better reducing agent; the excess can be removed by boiling.

3. Influence of Auxiliary Complexing Agents

Occasionally various carboxylic acids are added to prevent the precipitation of a metal ion (as an hydroxide) at the pH of the titration. Tartaric acid, oxalic acid, and citric acid are usually employed. We found that these substances also caused an increase in current, since they had a reducing effect on the oxide film, though in varying degrees (Figure 5). They also lowered the indication level for EDTA (Figure 6). These conditions do make it possible, however, to titrate almost any ion by choosing a pH at which complexing agents are unnecessary.

TABLE II. DIRECT TITRATION OF ION COMBINATIONS*

Ion combination	Ion	pH	log K_{eff}	Electrode	Note
Ba-Bi	Bi	2	8,6	Tl_2O_3	8, 9
	Ba	10	7,3		
Ba-Cd	Cd	4,5	9,0	Tl_2O_3	
	Ba	10	7,3		
Ba-Ce	Ce	4,5	8,9	Tl_2O_3	
	Ba	10	7,3		
Ba-Cu	Cu	4,5	11,2	Tl_2O_3	
	Ba	10	7,3		
Ba-Fe	Fe	3	13,9	Tl_2O_3	
	Ba	10	7,3		
Ba-Hg	Hg	4,5	11,3	Tl_2O_3	
	Ba	10	7,3		
Ba-La	La	6	10,6	Tl_2O_3	
	Ba	10	7,3		
Ba-Ni	Ni	4	10,1	Tl_2O_3	
	Ba	10	7,3		
Ba-Th	Th	4	14,5	Tl_2O_3	
	Ba	10	7,3		
Ba-Tl	Tl	2	8,5	Tl_2O_3	
	Ba	10	7,3		
Ba-Zn	Zn	6	11,7	Tl_2O_3	
	Ba	10	7,3		
Bi-Ba: see above					
Bi-Ca	Bi	2	8,6	Tl_2O_3	9, 12
	Ca	10	10,9		
Bi-Cd	Bi	2	8,6	MnO_2	12
	Cd	4,5	8,9		
Bi-Ce	Bi	2	8,6	MnO_2	12
	Ce	4,5	9,0		
Bi-Cu	Bi	2	8,6	MnO_2	12
	Cu	4,5	11,2		
Bi-La	Bi	2	8,6	MnO_2	12
	La	4,5	7,8		
Bi-Mg	Bi	2	8,6	Tl_2O_3	8, 9, 12
	Mg	10	8,2		
Bi-Ni	Bi	2	8,6	MnO_2	12
	Ni	4,5	11,0		
Bi-Sr	Bi	2	8,6	Tl_2O_3	8, 9, 12
	Sr	10	8,1		
Bi-Zn	Bi	2	8,6	MnO_2	12
	Zn	4,5	8,9		
Ca-Ba, Ca-Bi: see above					
Ca-Cd	Cd	4,5	8,9	Tl_2O_3	
	Ca	10	10,2		
Ca-Ce	Ce	4,5	8,9	Tl_2O_3	
	Ca	10	10,2		
Ca-Cu	Cu	4,5	11,2	Tl_2O_3	
	Ca	10	10,2		
Ca-Fe	Fe	3	13,9	Tl_2O_3	
	Ca	10	10,2		
Ca-Hg	Hg	4	11,3	Tl_2O_3	
	Ca	10	10,2		
Ca-La	La	4,5	7,8	Tl_2O_3	
	Ca	10	10,2		
Ca-Ni	Ni	4,5	11,0	Tl_2O_3	
	Ca	10	10,2		
Ca-Th	Th	3	12,4	Tl_2O_3	
	Ca	10	10,2		
Ca-Tl	Tl	2	8,5	Tl_2O_3	
	Ca	10	10,2		
Ca-Zn	Zn	4,5	8,9	Tl_2O_3	
	Ca	10	10,2		
Cd-Ba, Cd-Bi, Cd-Ca: see above					
Cd-Fe	Fe	2	11,5	MnO_2	
	Cd	4,5	8,9		
Cd-Hg	Hg	2	9,2	MnO_2	
	Cd	5	9,9		
Cd-Mg	Cd	5	9,9	Tl_2O_3	
	Mg	10	8,2		
Cd-Sr	Cd	5	9,9	Tl_2O_3	
	Sr	10	8,1		
Cd-Th	Th	2	9,5	MnO_2	
	Cd	5	9,9		
Cd-Tl	Tl	2	8,5	MnO_2	
	Cd	5	9,9		
Ce-Ba, Ce-Bi, Ce-Ca, Ce-Cd: see above					
Ce-Fe	Fe	2	11,5	MnO_2	
	Ce	4,5	9,0		
Ce-Mg	Ce	4,5	9,0	Tl_2O_3	
	Mg	10	8,2		
Ce-Sr	Ce	4,5	9,0	Tl_2O_3	
	Sr	10	8,1		
Ce-Th	Th	2	9,5	MnO_2	
	Ce	4,5	9,0		
Ce-Tl	Tl	2	8,5	MnO_2	
	Ce	4,5	9,0		
Cu-Ba, Cu-Bi, Cu-Ca: see above					
Cu-Fe	Fe	2	11,5	MnO_2	
	Cu	4,5	11,2		
Cu-Mg	Cu	4,5	11,2	Tl_2O_3	
	Mg	10	8,2		

* Translator's note: Commas in numbers represent decimal points

TABLE II (Continued)*

Ion combination	Ion	pH	log K_{eff}	Electrode	Note
Cu-Sr	Cu	4,5	11,2	Tl_2O_3	
	Sr	10	8,1		
Cu-Th	Th	2	9,5	MnO_2	
	Cu	4,5	11,2		
Fe-Ba, Fe-Ca, Fe-Cd, Fe-Ce, Fe-Cu: see above					
Fe-Co: Tab. 4					
Fe-La	Fe	2	11,5	MnO_2	
	La	5	8,8		
Fe-Mg	Fe	3	13,9	Tl_2O_3	
	Mg	10	8,2		
Fe-Ni	Fe	2	11,5	MnO_2	
	Ni	4,5	11,0		
Fe-Sr	Fe	3	13,9	Tl_2O_3	
	Sr	10	8,1		
Fe-Zn	Fe	2	11,5	MnO_2	
	Zn	4,5	8,5		
Hg-Ba, Hg-Ca, Hg-Cd: see above					
Hg-Ce, Hg-Co, Hg-Cu: see table 5					
Hg-Mg	Hg	4,5	11,3	Tl_2O_3	
	Mg	10	8,2		
Hg-Sr	Hg	4,5	11,3	Tl_2O_3	
	Sr	10	8,1		
La-Ba, La-Bi, La-Ca, La-Fe: see above					
La-Hg: see table 5					
La-Mg	La	6	9,5	Tl_2O_3	
	Mg	10	8,2		
La-Sr	La	6	9,5	Tl_2O_3	
	Sr	10	8,1		
La-Th	Th	2	9,5	MnO_2, Tl_2O_3	
	La	5	8,8		
La-Tl	Tl	2	8,5	MnO_2	
	La	5	8,8		
Mg-Bi, Mg-Cd, Mg-Ce, Mg-Cu, Mg-Fe, Mg-Hg, Mg-La: see above					
Mg-Co: see table 4					
Mg-Ni	Ni	4,5	11,0	Tl_2O_3	
	Mg	10	8,2		
Mg-Th	Th	3	12,4	Tl_2O_3	
	Mg	10	8,2		
Mg-Tl	Tl	2	8,5	Tl_2O_3	8
	Mg	10	8,2		
Mg-Zn	Zn	4,5	8,9	Tl_2O_3	
	Mg	10	8,2		
Ni-Ba, Ni-Bi, Ni-Ca, Ni-Fe, Ni-Mg: see above					
Ni-Sr	Ni	4,5	11,0	Tl_2O_3	
	Sr	10	8,1		
Ni-Th	Th	2	9,5	MnO_2	
	Ni	4,5	11,0		
Pb-Ba, Pb-Ca, Pb-Fe, Pb-Mg, Pb-Sr, Pb-Tl: see table 4					
Sr-Bi, Sr-Cd, Sr-Ce, Sr-Cu, Sr-Fe, Sr-Hg, Sr-La, Sr-Ni: see above					
Sr-Co, Sr-Pb: see table 4					
Sr-Th	Th	2	9,5	Tl_2O_3	8
	Sr	10	8,1		
Sr-Tl	Tl	2	8,5	Tl_2O_3	
	Sr	10	8,1		
Sr-Zn	Zn	4,5	8,9	Tl_2O_3	
	Sr	10	8,1		
Th-Ba, Th-Ca, Th-Cd, Th-Ce, Th-Cu, Th-La, Th-Mg, Th-Ni, Th-Sr: see above					
Th-Co: see table 4					
Th-Zn	Th	2	9,5	MnO_2	
	Zn	5	9,9		
Tl-Ba, Tl-Ca, Tl-Cd, Tl-Ce, Tl-La, Tl-Mg, Tl-Sr: see above					
Tl-Co, Tl-Pb: see table 4					
Tl-Zn	Tl	2	8,5	MnO_2	
	Zn	5	9,9		
Zn-Ba, Zn-Bi, Zn-Ca, Zn-Fe, Zn-Mg, Zn-Sr, Zn-Th, Zn-Tl: see above					
Zn-Hg: see table 5					

* Translator's note: Commas in numbers represent decimal points.

TABLE III. THE FOLLOWING ION COMBINATIONS CANNOT BE DETERMINED, BECAUSE THE LOG K_{eff} VALUES OF THE 2 IONS ARE SIMILAR

Al with	Cd, Ce, Co, Cu, La, Ni, Pb, Zn
Ba with	Ca, Mg, Sr
Bi with	Fe, Hg, Pb, Th, Tl
Ca with	Ba, Mg, Sr
Cd with	Ce, Co, Cu, La, Ni, Pb, Zn
Ce with	Co, Cd, Cu, La, Ni, Pb, Zn
Co with	Cd, Ce, Cu, La, Ni, Pb, Zn
Cu with	Cd, Ce, Co, La, Ni, Tl, Zn
Fe with	Hg, Th, Tl
Hg with	Bi, Fe, Ni, Pb, Th, Tl
La with	Cd, Ce, Co, Cu, Ni, Pb, Zn
Mg with	Ba, Ca, Sr
Mn with	Cd, Ce, Co, Cu, La, Zn
Ni with	Cd, Ce, Co, Cu, Hg, La, Pb, Tl, Zn
Pb with	Bi, Cd, Ce, Co, Cu, Hg, La, Ni, Zn
Sr with	Ba, Ca, Mg
Th with	Bi, Fe, Hg, Tl
Tl with	Bi, Cu, Fe, Hg, Ni, Th
Zn with	Cd, Ce, Co, Cu, La, Ni, Pb

a) Oxalic acid does not interfere in the alkaline range. In the acidic range it is oxydized at the oxide anode; it attacks the carboxyl groups.

b) Tartaric acid. At pH 10 the vicinal OH groups are oxydized; in the acidic range the oxidation is stronger (vicinal OH groups and carboxyl groups).

c) Citric acid is not oxydized at pH 10, since the carboxyl groups are ionized. The tertiary alcohol group does not react. Oxidation of the carboxyl groups and the resulting increase in current does not occur until the acidic range. /274

TABLE IV. ION COMBINATIONS IN WHICH ONE ION MUST BE DETERMINED THROUGH BACK-TITRATION (BT) *

Ion combination	Ion	pH	log K_{eff}	Electrode	Note
Al-Ba	Al (BT)	5	9,6	Tl_2O_3	13
	Ba	10	7,3		
Al-Bi	Bi	2	8,6	MnO_2	
	Al (BT)	5	9,6		
Al-Ca	Al (BT)	5	9,6	Tl_2O_3	13
	Ca	10	10,2		
Al-Fe	Fe	2	11,5	MnO_2	
	Al (BT)	5	9,6		
Al-Mg	Al (BT)	5	9,6	Tl_2O_3	13
	Mg	10	8,2		
Al-Sr	Al (BT)	5	9,6	Tl_2O_3	13
	Sr	10	8,1		
Al-Th	Th	2	9,5	MnO_2	
	Al (BT)	5	9,6		
Al-Tl	Tl	2	8,5	MnO_2	
	Al (BT)	5	9,6		
Ba-Co	Co (BT)	4,5	8,8	Tl_2O_3	10
	Ba	10	7,3		
Ba-Pb	Pb (BT)	6	13,2	Tl_2O_3	10
	Ba	10	7,3		
Bi-Co	Bi	2	8,6	MnO_2	10
	Co (BT)	4,5	8,8		
Ca-Co	Co (BT)	4,5	8,8	Tl_2O_3	
	Ca	10	10,2		
Ca-Pb	Pb (BT)	4,5	10,4	Tl_2O_3	12
	Ca	10	10,2		
Co-Fe	Fe	2	11,5	MnO_2	
	Co (BT)	4,5	8,8		
Co-Mg	Co (BT)	4,5	8,8	Tl_2O_3	
	Mg	10	8,2		
Co-Sr	Co (BT)	4,5	8,8	Tl_2O_3	
	Sr	10	8,1		
Co-Th	Th	2	9,5	MnO_2	
	Co (BT)	4,5	8,8		
Co-Tl	Tl	2	8,5	MnO_2	
	Co (BT)	4,5	8,8		
Fe-Pb	Fe	2	11,5	Tl_2O_3	8
	Pb (BT)	10	14,8		
Mg-Pb	Pb (BT)	4,5	10,4	Tl_2O_3	
	Mg	10	8,2		
Pb-Sr	Pb (BT)	6	13,2	Tl_2O_3	
	Sr	10	8,1		
Pb-Th	Th	2	9,5	Tl_2O_3	
	Pb (BT)	6	13,2		
Pb-Tl	Tl	2	8,5	Tl_2O_3	
	Pb (BT)	6	13,2		

*Translator's note: Commas in numbers represent decimal points.

Notes on Tables 2 - 4

Note 8. The Tl_2O_3 electrode must be solidly made (20 μA, 3 min), or the oxide film will slowly dissolve at pH 2.

Note 9. Only Bi can be titrated. A basic salt is precipitated when the solution is adjusted to pH 10, and the liberated EDTA interferes with the titration of the 2nd ion.

Note 10. Back-titration is necessary because direct titration would cause Co, Pb, and Mn to separate from the anode. There is then no indication of EDTA.

Note 11. Chloride interferes, because difficultly soluble BiOCl is formed.

Note 12. With the addition of tartaric acid (5 ml of 0.01 M solution).

Note 13. In this combination only Al can be determined. At pH 10 the Al-EDTA complex dissociates and EDTA is liberated.

TABLE V. ION COMBINATIONS WHICH, FOR EXPERIMENTAL REASONS, CANNOT BE TITRATED, ALTHOUGH THE LOG K_{eff} VALUES ARE DISSIMILAR.

Hg with	Al, Ce, Co, Cu, La, Ni, Zn
Mn with	Ba, Bi, Ca, Fe, Hg, Mg, Ni, Pb, Sr, Th, Tl, Zn

4. Addition of Masking Agents

Chelatometric titration (with metal indicators) has classically involved the use of various masking agents to eliminate the effect of interfering ions. Typical masking agents are cyanide, triethanolamine, tetren (tetraethylenepentamine) and pentene (pentaethylenehexamine). For the sake of thoroughness we have investigated the influence of these masking agents on the oxide anode, although — as was shown above — many interfering ions can be eliminated by choosing the proper pH.

a) Cyanide has been suggested as a masking agent for Cd, Co, Cu, Ni, Pb, Hg and Zn; for the formation constants, see Ringborm [3].

Figure 5, No. 6, shows that the addition of excess cyanide causes the current between the electrodes to fall. If EDTA is subsequently added to the solution, the current increases. This increase is less, however, than it would be if no cyanide were present (Figure 6, No. 1). In principle, therefore, it is possible to use cyanide in the masking of metal ions and then perform the titration with EDTA.

We explain the behavior of cyanide as follows: Cyanide first reduces a part of the oxide film, forming insoluble bonds with the reduced places. These partially prevent reoxidation. However, as we have previously shown, reoxidation is responsible for the increase in current after excess EDTA has been added.

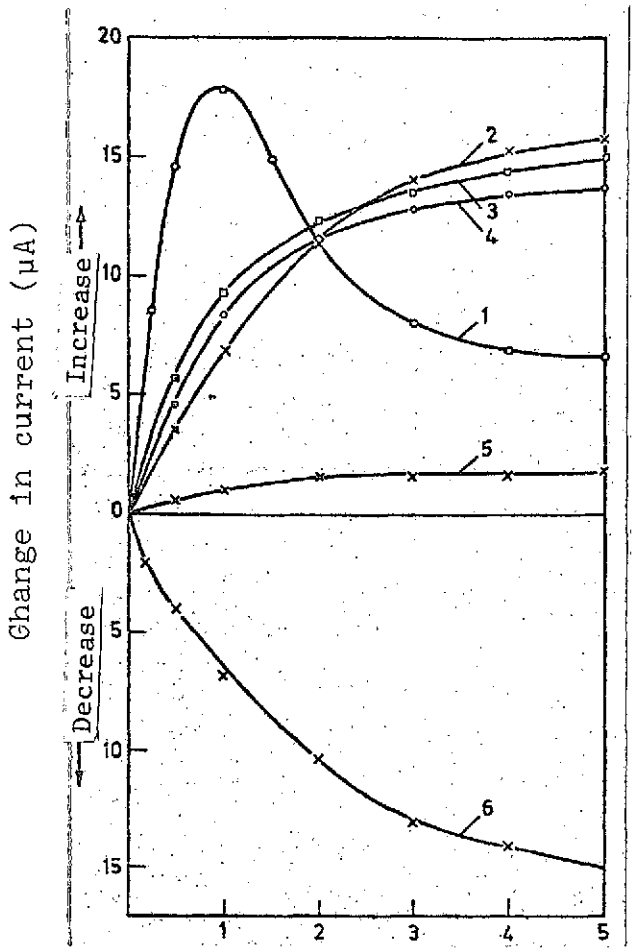

Figure 5. Change in current during the addition of complexing agents and masking agents while employing oxide electrodes.

1- EDTA, pH 10, Tl_2O_3 electrode; 2- oxalic acid, pH 4.5, PbO_2 electrode; 3- tartaric acid, pH 4.5, PbO_2 electrode; 4- triethanolamine, pH 4.5, PbO_2 electrode; 5- citric acid, pH 4.5, Tl_2O_3 electrode; 6- cyanide, pH 4.5, PbO_2 electrode.

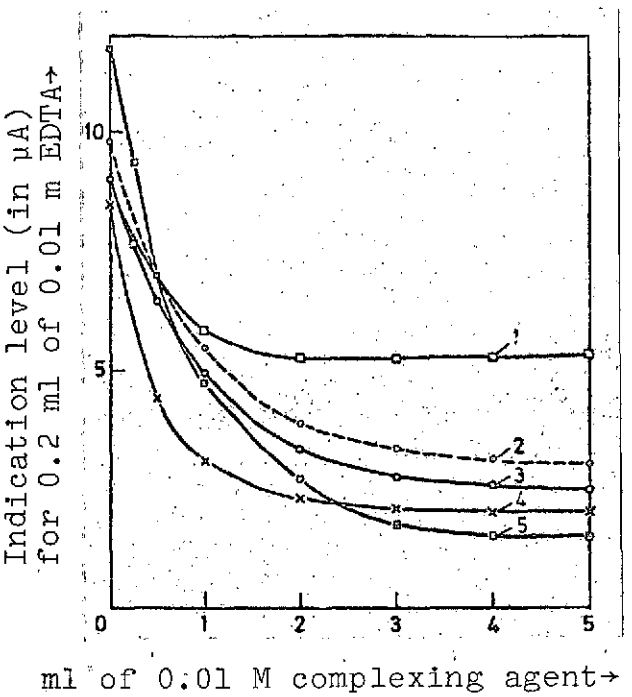

Figure 6. Change in the indication level of EDTA (0.2 ml of 0.01 M solution) in the presence of increasing amounts of masking agent (pH 4.5; PbO_2 electrode).

1- cyanide; 2- oxalic acid; 3- tartaric acid; 4- triethanolamine; 5- citric acid.

The addition of excess cyanide can be avoided by complexing all the aforementioned ions at pH 4.5 stoichiometrically with EDTA and then determining the desired alkaline earths at pH 10. /275 The complexation of the interfering ions as well as the titration itself are performed with a suitable oxide electrode (e.g., Tl_2O_3).

b) Triethanolamine has been suggested as a masking agent for Fe, Mn, Al, and Ti, in order to be able to determine the alkaline earths at pH 10. We found that triethanolamine increases the basic current; it is thus partially oxidized at the oxide anode. As more TEA is added, the indication level for EDTA is correspondingly lowered, and after 30 ml of 0.05 M TEA solution have been added, EDTA is no longer indicated. The use of triethanolamine as a masking agent can be avoided, however, this procedure being the same as for cyanide.

c) Tetren and penten. These compounds are used to mask Cd, Co, Cu, Fe, Hg, Mn, Ni, Zn and Pb in the determination of alkaline earths. They also damage the oxide electride, increase the basic current, and lower the signal level for EDTA. The masking procedure is the same as in (a) above.

We must conclude, therefore, that the masking agents usually employed in classical complexometric titrations are not suitable if we wish to use an oxide electrode as the end-point indicator. It is almost always possible, however, to complex interfering ions stoichiometrically with EDTA by choosing a suitable pH, and then titrate the ion desired.

Discussion

As has been shown, the oxide electrode is a very versatile tool in determining metal ions with EDTA. One particular advantage is that it indicates EDTA over a wider range of pH. It is thus possible to determine numerous ions when present together in a solution. It is usually unnecessary to add masking agents or auxiliary complexing agents.

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